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Durability assessment and physical properties investigation of modified petung bamboo (Dendrocalamus asper) as resulted on acetylation, assisted by supercritical CO_2

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Abstract

Due to its ecological benefits, bamboo is considered as attractive material. Recently, conventional bamboo modification in industry consumes time and chemicals. Supercritical fluid technology contributes to overcome these disadvantages. This process was performed in a batch impregnation with a statistical method. In this study, durability tests over a period of 32 weeks confirm that acetylated (un)-extracted bamboos regarded as durable material with mass loss ratio median (X) of 0.24-0.25. Additional the results of water sorption isotherm and the fibre saturation points are illustrated, as well as the crystallinity index.

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Keywords: Durability assessment, sorption isotherm, fiber saturation point, acetylation, supercritical CO_2

1. Introduction

At first glance, bamboo is a fast growing grass which is very well known in Asia to be one of the most booming materials for the future [1]. It is proved, that bamboo is one of the most sustainable materials, which can bind atmospheric carbon dioxide in a very high density as biomass [2-4]. Indonesia has the highest genetic diversity of bamboo species in South East Asia [3]. Approximately 1250 bamboo species have been recorded in the world and in

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Indonesia about 135 species can be found, belonging to 21 different genera [5]. Undoubtedly, bamboo could help to overcome the devastation of tropical forest area in Indonesia. Approximately 0.5 million hectare are deforested annually to supply the wood demand in Indonesia and to convert forest land into industrial agriculture land, where e.g. palm oil plantations are installed [6]. As a consequence, the Indonesian government is supporting the substitution of timber with other ligno-cellulosic materials, such as bamboo [7].

Petung bamboo (Dendrocalamus asper) is one of the most widely spread bamboos in Indonesia [5]. Petung bamboo is usually used as construction material, for music instruments, water-pipes, furnitures, agriculture-equipment and hand-crafts. The culm is 20 m tall and 10-18 cm in diameter. The internode is 40- 60 cm with a wall thickness around 11-18 mm [8]. Sugiyanto (2006) has examined the chemical properties of the bamboo species Dendrocalamus asper. It mainly consists of cellulose, lignin, and pentosan approximately 52.9, 24.8, and 18.8w% respectively [9]. Beside these main components Bamboo consists of minor components such as lipophilic extractives [10]. Bamboo has a higher cellulose contents than wood [11].

The bamboo culm impregnation was studied, based on wood impregnation using acetic anhydride with supercritical CO_2 as carrier media [12]. This new process is an alternative eco-friendly method to protect bamboo from biodegradation and to enhance the durability of bamboo. Chemical modification as an innovative strategy for the environmental-friendly protection of bamboo was accomplished by a reaction between acetylating agents with the major bamboo component. Bamboo has a different structure compared to wood, which makes it very difficult to penetrate the surface of bamboo by any liquid [13]. Due to these difficulties of classical techniques, a new process using supercritical CO_2 as carrier media was developed. CO_2 is known to have a very high diffusivity [11] and therefore it seems to be suitable to impregnate the very dense bamboo structure. The composition of bamboo prominently comprises of the cellulose, hemicellulose, and lignin. Cellulose in bamboo exhibits as crystalline parts of bamboo, while the hemicellulose and lignin represent as amorphous parts. In bamboo, hemicellulose mainly represents as xylan which is instable parts of hemicellulose [14].

Previous research works have elaborated the physical, chemical and thermal-mechanical properties of bamboo [9, 15-16]. The suitability of bamboo as construction material is demonstrated based on physical properties, such as the equilibrium moisture content and the fiber saturation point. These properties are closely influenced by the amount of water.

This study used a statistical design of experiment approach, by using Design Expert 8.0.6 (Stat-Ease, Inc), in order to obtain the optimum results for the bamboo modification, assisted by supercritical CO_2. A statistical approach was executed using factorial design three variables, i.e. pressure, temperature, and time with total 32 number of experiments and 4 replicates in order to have probability 92.7 %. After the impregnation, the durability of the modified bamboos was investigated based on the standard ENV 807 method [17], which helps to classify the products durability. The durability test was supported by additional investigations, focusing on the sorption of water, the fiber saturation point, and the crystallinity index of the modified bamboos.

1.1. Sorption isotherm

The chemical structure of bamboo with its high amount of hydroxyl groups is leading to a natural hydrophilicity and therefore to the sorption of moisture. The modification of bamboo by impregnation processes is focusing on the replacement of the hydroxyl groups with other less polar components [18]. To get an insight into the structure of the modified bamboo, the sorption and desorption of water is an adequate method. The sorption process is reversible, but normally a hysteresis is observed. The amount of water adsorbed by dry cellulosic materials is lower than the amount of water which is released during the desorption. The hysteresis of the sorption and desorption can be seen in Fig 1. Due to the composition, sorption isotherm of bamboo is regarded similar with wood sorption isotherm which described sigmoid shape of the type II sorption isotherm [19].

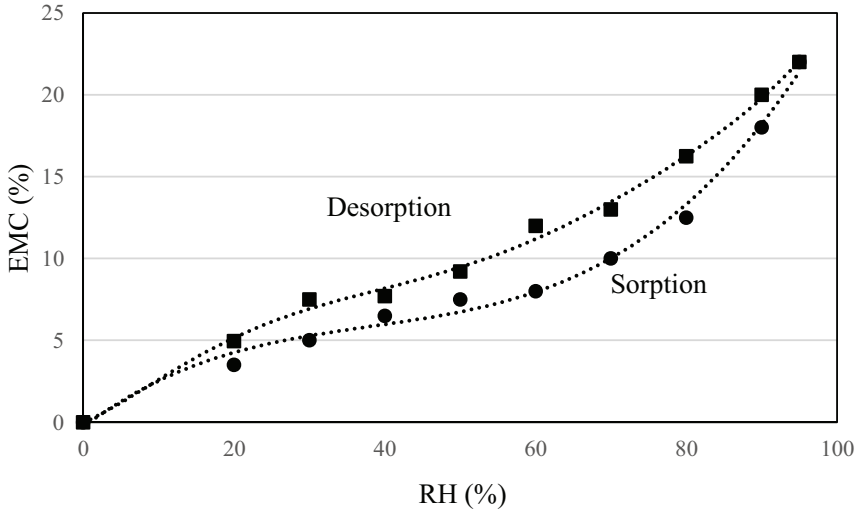

Fig. 1 Sorption isotherm with hysteresis between sorption and desorption of water [18].

1.2. Fiber saturation point

Recently, the fiber saturation point (hence FSP) of Indonesian bamboo are unavailable in literature. Therefore the FSP measurements of Indonesian bamboo were performed in this research. The maximum amount of water can be held in the cell wall corresponding to the relative humidity. The water is attached over the hydroxyl groups in cellulose, hemicellulose and lignin or bound by capillary forces [20]. The existing water inside bamboo is considered to be divided into three distinct forms, i.e. liquid water (free water as freezing water) and water vapor fill in the voids and bound water. Bound water exists in the cell wall as non-freezing water [21]. The existence of water forms in bamboo/wood pores can be illustrated in Fig. 2**.** The disappearing liquid water in the voids denotes moisture content of bamboo at FSP (middle of Fig. 2).

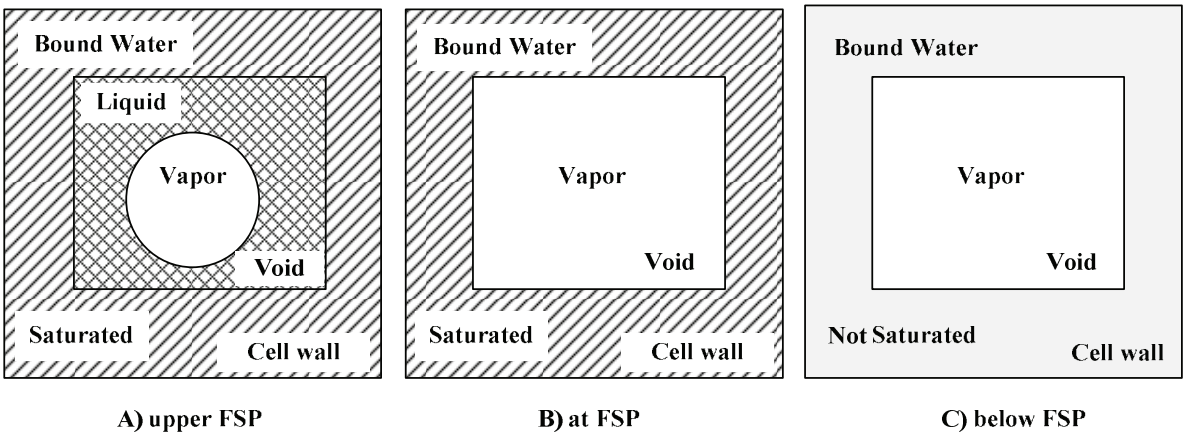

Fig. 2 Three forms of water in bamboo/wood at different conditions: upper FSP (left); at FSP (middle); below FSP (right) [21]

The FSP is measured by the use of a DSC (differential scanning calorimeter) which allows to quantify the amount of non-freezable water. Due to the facts that only free water in the voids can be frozen. It is possible to

determine the melting enthalpy of freezing water by presenting an endothermic peak at temperature of melting of water (273.15 K).

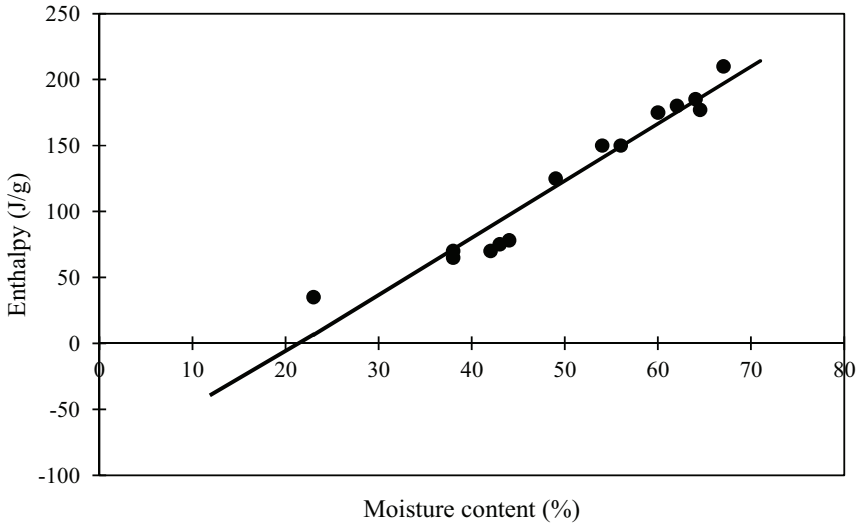

Fig. 3 Measurement of the FSP value at zero- the enthalpy of melting by extrapolation [22]

Moreover, melting enthalpies values obtained from DSC are used to calculate the proportion of non-freezing water by extrapolation of plotting of observed melting enthalpy versus water content using least square regression. The FSP is obtained when the melting enthalpy is zero where the extrapolation line cross the ordinate at zero melting enthalpy. This phenomenon can be represented in Fig. 3.

1.3. Durability assessment

When testing the durability according to the European standard ENV 807 method [17], modified bamboo is brought into contact for 32 weeks with unsterile commercial soil to determine the natural durability of the modified bamboo. The moisture content and the mass loss are determined as response data of this durability test. To compare the samples the quotient of the median value of the mass loss of the single samples to the median values of the reference material is formed in Eq. 1 [17]. The reference material is the unmodified bamboo.

$$X = \frac{median\,value\ \text{of}\ mass\ loss\ for\ the\ test\ material\ specimens}{median\,value\ \text{of}\ mass\ loss\ for\ the\ \text{reference}\ material\ specimens} \tag{1}$$

The mass loss can be calculated with the following equation [17].

$$Mass\,loss(\%) = \frac{mass\ of\ bamboo_{initial} - mass\ of\ bamboo_{dried}}{mass\ of\ bamboo_{initial}}\ x\ 100 \tag{2}$$

According to the European standard, EN 350-1 [17], five different classes of durability can be defined. The criteria for these classes are given in Table 1.

Table 1 Criteria for the durability class [17]

Durability Class	Criteria EN 350-1	Definition
1	X<0.15	Very durable
2	0.15<X≤0.3	Durable
3	0.3<X≤0.6	Moderately durable
4	0.6<X≤0.9	Slightly durable
5	X>0.9	Not durable

To support the results from the durability test, the crystallinity index of bamboo cellulose was predicted via FTIR measurements. There are four methods to determine this crystallinity index [23]. The simplest method is using the relative peak heights of the spectra. The results investigated by FTIR spectroscopy is giving to relative values due to this method is not the absolute measurement technique. Moreover, the spectra always consist of crystalline and amorphous regions contributions [23]. The crystallinity index denotes the relative amount of crystalline material in cellulose. This investigation of the crystallinity index was aimed to ensure that water cannot penetrate the modified bamboo due to the crystalline domains [24]. As a result of this modification which was conducted on high temperature (393 K), it was deduced that hemicellulose and the less ordered cellulose decay without changing of crystalline structure of cellulose and following increase the crystallinity index of cellulose [25].

2. Material and Methods

2.1. Material

Mature bamboo culms used in this study were delivered from Sumedang, West-Java, Indonesia. These green bamboos were cut into slices with a size of 50 mm x 30 mm x 15 mm in order to ease the drying and the storage. The drying was made in accordance to ISO 22157-1 (2004) at temperature 378 K for 24 hours [26] to reduce the moisture content from 43-60% to 5-10%. Some bamboo samples were extracted with CO_2 before the impregnation process in order to enhance the permeability. The supercritical extraction procedure was briefly provided in the literature [27]. Such prepared bamboo slices have been used for the batch impregnation process assisted by supercritical CO_2. CO_2 was provided by YARA with a purity of 99.9v%. Acetic anhydride was purchased by Acros Organic with purity of more than 99w%. A salt solution of K_2SO_4 was used to maintain the relative humidity during the durability test [28]. The salt was provided from Sigma-Aldrich with ≥ 99.0% in purity.

2.2. Methods

2.2.1. The sorption isotherm

The adsorption and desorption of water vapor on the samples were measured with BELSORP aqua3 (BEL Japan, Inc) at Rubotherm. Belsorp aqua3 measures the vapor adsorption based on the constant volumetric method. This method is extensively used and much easier than various adsorption measurements methods. With this method, the adsorbed amount is calculated from the gas pressure change in system. The sorption experiments were made at a fixed temperature of 313 K. For the adsorption the relative humidity was varied from 0.025 to 0.95 in steps of 0.025. To reach equilibrium each point was hold for about 800 seconds. The desorption was measured in the interval from 0.9 to 0.05 in steps of 0.1 and a temperature of 313 K.

2.2.2. Fiber saturation point

All measurements were conducted with a diffential scanning calorimetry (DSC 131 Evo by Setaram Instrumentation, France) under nitrogen flow at pressure of 2.10^5 Pa to cell. The lower temperature during the measurements was maintained by using liquid nitrogen. Before measuring, the samples were prepared by cutting small pieces of the specimens which were appropriate into the small sample container of the DSC. These oven dried samples were weighed and then the samples were contacted with cotton wool, which was saturated with water in

order to control the moisture content [22]. The water saturated samples were weighed in order to obtain the moisture content of samples. The moisture content was determined by gravimetric. Directly prior to the DSC measurement samples were sealed by pressing the small container lid, then lid was punctured. The weight of each investigated sample is maximum 10^{-5} kg. The samples were weighed before and after the measurement. The samples with adjusted moisture content were cooled to 223.15 K using liquid nitrogen and afterwards heated to 323.15 K with a scanning rate of 10 K/min [22]. During the heating, the melting enthalpy was measured for the frozen water. The endotherm peak of the melting process was only observed for water contents above the FSP. The observed melting enthalpy ($\Delta Hm,obs$) was plotted against the water content. Later, the moisture content, where the enthalpy of melting becomes zero can be obtained by extrapolation.

2.2.3. Durability assessment

Modified bamboos were put in unsterile commercial soil on a petri disk. Afterwards the samples were placed in a desiccator having a salt solution in the bottom part. With this salt, K_2SO_4, the relative humidity was controlled. This specific salt was used to obtain a relative humidity of 97% [28]. The desiccator was placed in a room maintained at 303 K. All samples stay in the desiccator for 32 weeks. The weight of the dried samples was determined prior and post of the treatment using a balance with an accuracy of 10^{-4} kg (Mettler Toledo, Switzerland) in order to obtain the mass loss (Eq. 2) The quotient of median of these both weights is used to obtain the X-value given in Eq. (1). In addition information FTIR spectra of the samples after treatment were made in order to obtain the crystallinity index. For these measurements a FTIR (Alpha Bruker Germany) in the wave number region of 650 – 4000 cm^{-1}, with a spectral resolution of 4 cm^{-1} for 24 scans was used. The peak height of the spectra was determined based on Pandey & Pitman method [29]. Nelson & O'Connor propose the methodology to predict the total crystalline index (hence TCI) [30]. Determination of TCI of bamboo samples were calculated by using the peak height ratio at 1372 and 2900 cm^{-1} (H_{1372}/H_{2900}, C-H bending/C-H stretching) in order to predict crystallinity index of a mixture of cellulose types I and II. The band ratio of H_{1429}/H_{897} represents the lateral order index (hence LOI) [30].Furthermore, the assignments of a mixture of two crystalline modifications, i.e. cellulose I_α and I_β, are addressed to the absorption bands at 750 and 710 cm^{-1} (H_{750}/H_{710}), respectively [31-32]. The spectra of 2900 cm^{-1} serves as the internal standard correction and does not depend on the crystallinity changes. The 1372 cm^{-1} spectra refers to measure the intensity according to the crystallinity change [31].

3. Results and Discussion

3.1. Sorption isotherm

In Figure 4 the water sorption and desorption isotherms of un-modified and acetylated bamboo are shown. As declared in the previous section that the sorption of water of bamboo can be depicted by sigmoid shape of the type II isotherm. It is considered that the monolayer-multilayer physisorption is enhanced up to the saturation pressure [19]. Moreover this type of sorption is repeatedly taken to represent a monomolecular water which related to the primary sorption sites, OH groups and a multilayer component where the non-freezing bound water in the cell wall are barely well connected with the fixed cell wall OH group [18]. As expected, a hysteresis between adsorption and desorption can be observed. The observed hysteresis represented in this following picture that the higher moisture content during desorption clarified in terms of hydrogen bondings between the cellulose of bamboo being collapse and replaced hydrogen bond between cellulose and water molecules. During the desorption, they are reformed with a lag resulting higher moisture content [19]. The unmodified bamboo sample can densely more absorb moisture than the modified bamboo due to acetylation between OH groups of the cellulose of bamboo with moieties acetyl from acetic anhydride.

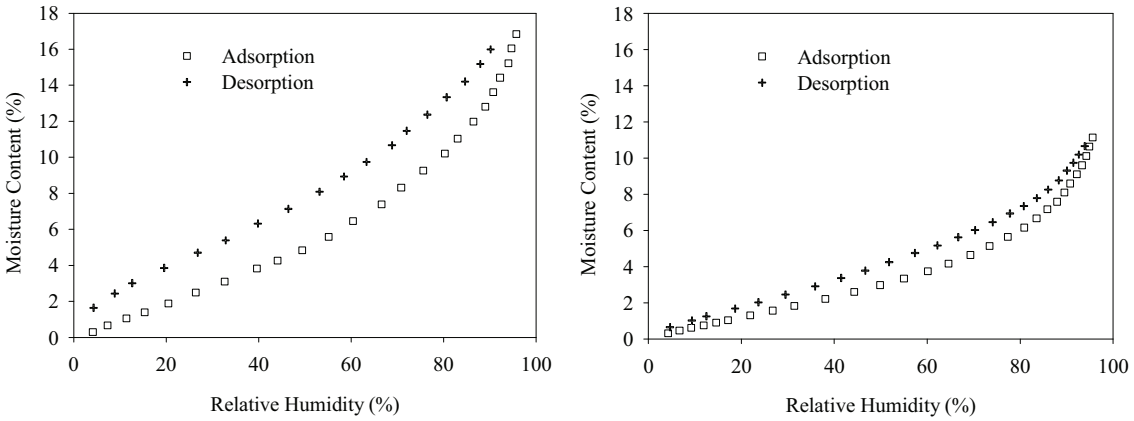

Fig. 4 The sorption isotherm of water for unmodified petung (left); bamboo acetylated petung bamboo (right). at temperature of 310 K

In addition the ratios of the adsorption and desorption values of moisture content (A/D ratio) were calculated (Figure 5) [33]. The result indicated that the moisture content of acetylated bamboo during desorption was lower than that of the unmodified bamboo. As consequence, the A/D ratio of the acetylated bamboo was approximately more than 0.8 according to the lower of desorption value of the acetylated of bamboo. Moreover the sorption isotherm of acetylated bamboo shows a narrow hysteresis between sorption and desorption. This is caused by the reaction of the acetic anhydride with the hydroxyl groups of the bamboo. Resultant the number of hydrogen bonds between the water and the bamboo structure is reduced.

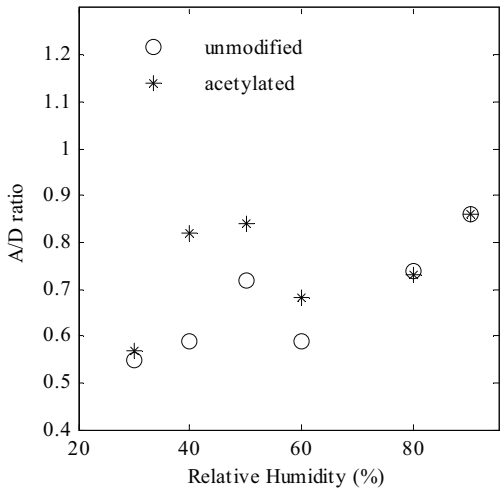

Fig. 5 The quantification of sorption isotherm (A/D ratio) for unmodified and acetylated petung bamboo (*Dendrocalamus Asper*) at temperature of 310 K.

3.2. Fiber saturation point

The results of the fiber saturation point measurements are shown in Table 2. Beside the unmodified bamboo, the CO_2-extracted and the acetylated bamboo were investigated. For the unmodified bamboo the saturation is achieved at 29% as FSP. The carbon dioxide extraction is leading to a higher water uptake of the fibers [34]. Here 37% are necessary to obtain free water. The positive effect of the acetylation becomes obvious with the decreased value of 18%. The acetylation seems to improve the hydrophobicity of the bamboo fibres. The reduced FSP of wood also was revealed by Hill, et.al. [35].

Table 2 Fiber saturation points of unmodified, extracted and acetylated bamboo

Unmodified un-extracted	Extracted	Acetylated
29%	37%	18%

The fiber saturation point measurements, done with the DSC device, are illustrated in Figure 6. As the measured data are highly non-linear, it is difficult to extrapolate to zero-enthalpy line to obtain the FSP-points. The results indicated that determining the FSP of bamboo using DSC methods [22] may not be appropriate to determine the non-freeze water of bamboo with moisture content of bamboo up to 50%. Therefore the enthalpies of melting were obtained higher than that of wood. To verify the results additional measurements with the FTIR were made. These results giving a relative crystallinity of the samples, are discussed in the following section.

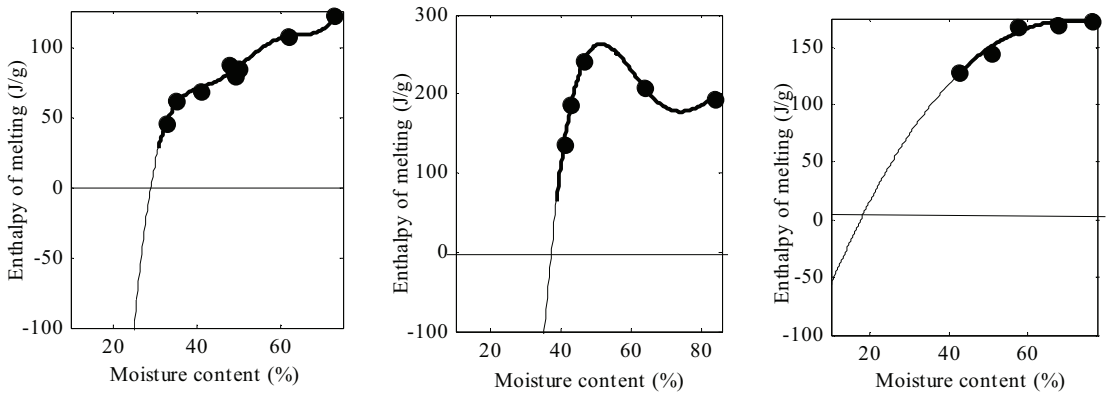

Fig. 6 Extrapolation of melting enthalpy for (a) unextracted bamboo; (b) extracted bamboo; (c) acetylated bamboo.

3.3. Durability assessment

The results of the durability test are given in Table 3. According to Table 3 the samples are in the category of "durable" after a period of 32 weeks. The un-extracted acetylated bamboo shows slight higher of the X value than the extracted acetylated bamboo after 32 weeks. In the first assessment ($X_{16\ weeks}$), the acetylated un-extracted bamboo run into huge loss in mass. The extractives of petung bamboo comprise of polar and non-polar extractives [9, 10]. Therefore, it was postulated that removing extractives prior to modification of bamboo can enhance the permeability of bamboo in order to ease diffusion and the fluid transport within bamboo. However, extractives can act as natural resistance, while the other components of extractives such as triglycerides, long chain fatty acid, steryl ester can be completely degraded by all the fungi [36].

Table 3 Classification of modified bamboos according to EN 350-1

Samples	$X_{16\ weeks}$	$X_{32\ weeks}$	Category
Acetylated un-extracted	0.59	0.25	Durable
Acetylated extracted	0.25	0.24	Durable

In this research, the change of crystallinity of cellulose of TCI and LOI in six bamboo samples was analyzed by using different intensity ratio between IR absorption including peak height in the absorbance spectra. Moreover, the crystallinity prediction have been measured the ratio of H_{750}/H_{710}, as can be seen in Table 4-6.

Table 4 Total crystallinity index of un-extracted acetylated bamboos

Samples	Un-extracted Acetylated					
H_{1429}/H_{897}	3.2	2	2	2	3.5	3
H_{1372}/H_{2900}	1.2	2	1	2	1.1	1.7
H_{750}/H_{710}	0.5	1	0.5	0.8	0.4	1

Table 5 Total crystallinity index of extracted acetylated bamboos

Samples	Extracted Acetylated					
H_{1429}/H_{897}	1	2	3	3.3	5.5	2
H_{1372}/H_{2900}	2	2	1	3.1	1.8	2.1
H_{750}/H_{710}	0.4	0.8	1	1	0.8	0.6

Table 6 Total crystallinity index of unmodified unextracted bamboos

Samples	Unmodified unextracted		
H_{1429}/H_{897}	3.3	2	3
H_{1372}/H_{2900}	0.3	0.3	1
H_{750}/H_{710}	-	-	1

The crystallinity value (TCI and LOI) of extracted acetylated and un-extracted acetylated shown no significant different in values. It is known from literature [37] that removing of extractives in wood was confirmed that no changing in the crystallinity but only increase in strength of modified wood. Moreover, the unmodified unextracted bamboos led higher value in the LOI due to some extractives could allow protecting naturally for decay; nevertheless no peak height was revealed in the crystallinity mixture of cellulose (H_{750}/H_{710}). In the previous mentioned, some extractives of bamboo can be destroyed by microorganism [36].

Conclusion

This paper investigates the durability assessment of modified bamboo samples compared to other kind of bamboo samples over a period of 32 weeks. These findings briefly provided the results of sorption isotherm, fiber saturation point, and crystallinity of bamboo samples post durability assessment. Sorption isotherm of modified bamboos presented with a narrow hysteresis resulted by reduction of hydrogen bonding between water and bamboo due to acetylation. Determination of fiber saturation points considerably were affected by the presence of extractives. However, extrapolation of enthalpy of melting favorable resulted nonlinear. Moreover, the extractives also inferred the mass loss in durability test and determination of the crystallinity index. Undoubtedly, extractives can naturally govern the modified bamboo prolonging the durability but also such extractives could be decay by microorganism resulting increase the mass loss.

Acknowledgements

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